

Rheology of Rodlike Polymers
in Isotropic and Liquid Crystalline Phases

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Introduction

Rheological properties of solutions of rodlike polymers change dramatically with concentration (1). At very low concentration, the solution is nearly a Newtonian fluid with low viscosity. As the concentration increases, the viscosity increases rapidly and there appears marked nonlinear viscoelasticity. With further increase in concentration the solution forms the liquid crystalline phase which has lower viscosity than that of the isotropic phase. The purpose of this paper is to derive a constitutive equation for such system on the basis of the molecular kinetic theory (2).

Theory

We consider the solution of rodlike polymers in the concentration region

$$\phi > 1/p^2 \quad (1)$$

where ϕ is the volume fraction of the polymer and p , the axis ratio. The microscopic view of such system is illustrated in Fig.1.

To derive the constitutive equation, we first write down the kinetic equation for the orientational distribution function $f(\underline{y};t)$ (\underline{y} being the unit vector along an arbitrary chosen test polymer).

$$\frac{\partial f}{\partial t} = \underline{\mathcal{R}} \cdot \tilde{\mathcal{D}}_r \cdot [\underline{\mathcal{R}} f + \frac{f}{k_B T} \underline{\mathcal{R}} \cdot \mathcal{V}_{SCF}(\underline{y})] - \underline{\mathcal{R}} \cdot (\underline{y} \times \underline{\kappa} \underline{y}) \quad (2)$$

where $\underline{\mathcal{R}} = \underline{y} \times \partial/\partial \underline{y}$, and $\underline{\kappa}$, the velocity gradient tensor. Though eq.(2) is similar to the usual rotational diffusion equation in dilute-solution-theory, it differs from that in two important points: (i) In concentrated solution, the rotational diffusion occurs much more slowly than in dilute solution since the rotation of each polymer is hindered by the surrounding ones. This effect is accounted for by the effective diffusion constant $\tilde{\mathcal{D}}_r$ which was predicted by the "reptation-rotation" model (3). (ii) The tendency that the polymers align in the liquid crystalline phase is taken into account by the mean field potential $\mathcal{V}_{SCF}(\underline{y})$.

Next we express the macroscopic stress tensor $\underline{\sigma}$ in terms of $f(\underline{y};t)$ as

$$\underline{\sigma} = \frac{\rho RT}{M} \left\{ \langle 3\underline{y}\underline{y} - \underline{I} \rangle + \langle (\underline{y} \times \underline{Q}^V_{SCF})\underline{y} \rangle / k_B T \right\} \quad (3)$$

where ρ is the polymer density and M , the molecular weight. Using eqs.(2) and (3), one can calculate $\underline{\sigma}$ for given $\underline{\kappa}(t)$. To simplify the analysis, however, we take further step: defining the order parameter tensor as

$$\underline{S} = \langle \underline{y}\underline{y} - \underline{I}/3 \rangle \quad (4)$$

we derive a closed equation for \underline{S} by using a certain decoupling approximation. The result is

$$\frac{\partial \underline{S}}{\partial t} = \underline{F}(\underline{S}) + \underline{G}(\underline{S}) \quad (5)$$

$$\underline{F}(\underline{S}) = -6\overline{D}_r \left[\left(1 - \frac{U}{3}\right)\underline{S} - U(\underline{S} \cdot \underline{S} - \frac{1}{3}\underline{S}:\underline{S}) + U\underline{S}(\underline{S}:\underline{S}) \right] \quad (6)$$

$$\underline{G}(\underline{S}) = \frac{1}{3}(\underline{\kappa} + \underline{\kappa}^\dagger) + (\underline{\kappa} \cdot \underline{S} + \underline{S} \cdot \underline{\kappa}^\dagger - \frac{2}{3}\underline{\kappa}:\underline{S}) - 2\underline{S}(\underline{\kappa}:\underline{S}) \quad (7)$$

where $U = 3\phi/\phi^*$ (ϕ^* being the critical volume fraction above which the isotropic phase becomes unstable), and \overline{D}_r is related to the rotational diffusion constant D_{r0} in infinite dilution as

$$\overline{D}_r = \nu D_{r0} (\phi p^2)^{-2} \left[1 - \frac{3}{2}\underline{S}:\underline{S}\right]^{-2} \quad (8)$$

(ν is a certain numerical constant of order unity.) The stress tensor $\underline{\sigma}$ is related to \underline{S} as

$$\underline{\sigma} = \frac{\rho RT}{2M\overline{D}_r} \underline{F}(\underline{S}) \quad (9)$$

Some of the consequences of the above equations are:

- (i) The steady state viscosity takes maximum around ϕ^* (see Fig.2), in agreement with experiments (4,5).
- (ii) The shear modulus in the rubbery region, when plotted against ϕ , has two maximums; one in the isotropic phase and the other in the liquid crystalline phase.

References

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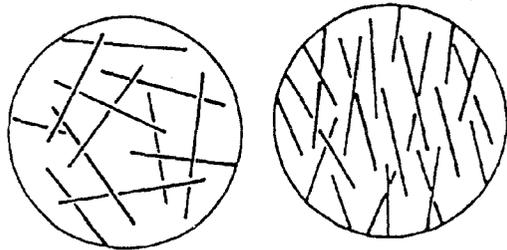


Fig.1

$1/P^2 < \phi < \phi^*$

$\phi^* < \phi$

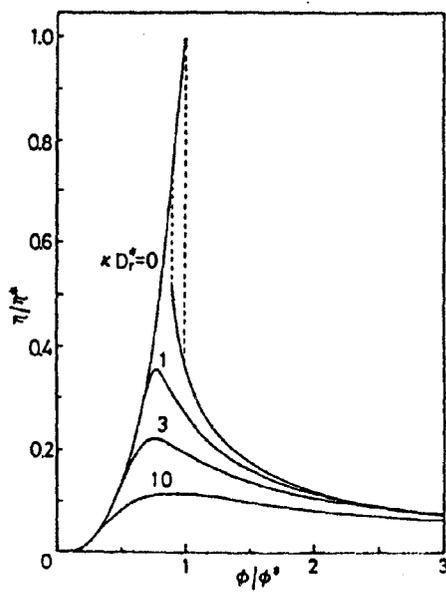


Fig.2

The steady state viscosity $\eta(\kappa)$ is plotted against concentration for various shear rate κ .